# MINERAL SPRINGS OF THE DAYLESFORD DISTRICT

By R. J. W. McLaughlin and Jennifer J. Macumber

Geology Department, University of Melbourne

## Abstract

Mineral springs in the Daylesford region and several from other areas have been analysed for Na, K, Li, Ca, Mg, Fe, Mn, B, $CO_3$, $SiO_2$, $PO_4$, $SO_4$, Cl, Br, and traces of several other minor elements have been detected. The ratios of the major cations are similar to those of normal river and surface waters. This evidence, as well as the low values for silica and boron, indicates an origin from percolating meteoric waters, with no contribution from volcanic fumaroles despite the close association with basalt.

## Introduction

The origin of the highly carbonated spring waters in and about the Daylesford region has interested various workers (Newbery, 1867; Skeats, 1914; Whitelaw & Baragwanath, 1923). While the general opinion has been that these spring waters are due to upward movement of ground water along fissures, the frequent association of springs with late Tertiary basalt has raised the possibility of some contribution from volcanic activity. Because of chemical differences which might be expected if this latter were true, various elements have been determined. Analytical methods used were: Calcium and magnesium, E.D.T.A. (Welcher, 1958); sodium and potassium, flame photometry (Vogel, 1961); iron, silica, phosphate, colorimetry (Mullin & Riley, 1955; Shapiro & Brannock, 1962); lithium, manganese and other trace cations, atomic absorption spectroscopy (Willis, 1963); chloride, bromide, carbonate, various titrimetric procedures (Wilson & Wilson, 1962); sulphate, turbidimetry (Vogel, 1961).

The samples were collected as follows: Nos. 1-7, 10 November, 1964; Nos. 8-22, 3 January, 1965. The various elements were estimated as rapidly as possible. Waters were not filtered, since this caused loss of carbon dioxide and precipitation of hydrated $R_2O_3$. Samples were taken after standing 24 hours to permit settling. After initial determination of chloride, bromide, boron (as borate) and carbonate, the waters were acidified with hydrochloric acid to prevent precipitation, and the remaining constituents then determined. Localities sampled have been shown in Fig. 1 and listed in Table 1.

## Results

Concentration in parts per million for fourteen elements has been given in Table 1. Variability has not been investigated in detail, but some indication has been given in Table 2 for several springs which have been sampled at different times during a four year period. The deviation is surprisingly small, considering the variability of the Ordovician shales and sandstones through which the springs rise.

The practice of reporting the various salts as a percentage of a dry weight has not been used in this investigation because of the excess carbon dioxide. Although in the table the carbonate content is given as $CO_3$, there will be a variety of species, $CO_3^{2-}$; $HCO_3^-$ and $CO_2$. The major cations are calcium, magnesium and

| Element | 1 | 4 | 5 | 6 | 7 | 8 | 9 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na | 150 | 435 | 445 | 150 | 200 | 310 | 195 | 360 | 140 | 280 | 295 | 250 | 87.5 | 225 | 520 | 425 | 460 | 490 |
| Ca | 68 | 130 | 152 | 54 | 92 | 141 | 154 | 97 | 166 | 201 | 83 | 140 | 85 | 194 | 252 | 177 | 168 | 135 |
| Mg | 62 | 114 | 122 | 112 | 145 | 144 | 126 | 93 | 148 | 174 | 87 | 124 | 96 | 189 | 235 | 207 | 274 | 406 |
| K | 37 | 126 | 137 | 23 | 68 | 10 | 7 | 18 | 5 | 12 | 10 | 7 | 6 | 7 | 11 | 7 | 8 | 18 |
| Li | 0.1 | 0.5 | 0.2 | 0.1 | 0.2 | 0.5 | 0.2 | 0.3 | 0.3 | 0.3 | 0.2 | 0.2 | 0.1 | 0.1 | 0.3 | 0.2 | 0.4 | 0.01 |
| Fe | 15 | 5 | 6 | 23 | 9 | 8 | 15 | 7 | 8 | 9 | 6 | 9 | 9 | 7 | 13 | 8 | 9 | 5 |
| Mn | 0.5 | 0.3 | 0.3 | 0.3 | 0.1 | 0.2 | 0.5 | 0.1 | 0.3 | 0.1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.5 | 0.3 | 0.3 | 0.2 |
| $CO_3$ | 363 | 893 | 935 | 389 | 622 | 855 | 658 | 802 | 725 | 1070 | 679 | 775 | 422 | 832 | 1298 | 919 | 943 | 1256 |
| $SO_4$ | 13 | 8 | 8 | 6 | 6 | 26 | 54 | 5 | 6 | 7 | 5 | 8 | 14 | 7 | 57 | 143 | 167 | 46 |
| Cl | 43 | 67 | 23 | 123 | 75 | 48 | 63 | 38 | 20 | 20 | 35 | 42 | 30 | 175 | 255 | 306 | 443 | 503 |
| Br | 0.6 | 0.2 | 0.3 | 0.4 | 0.2 | 0.3 | 0.4 | 0.2 | 0.4 | 0.4 | 0.6 | 0.4 | 0.6 | 0.4 | 1.1 | 1.2 | 1.3 | 2.8 |
| B | 0.4 | 0.7 | 0.7 | 0.6 | 0.3 | 0.2 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.3 | 0.1 | 0.1 | 0.2 | T | 0.2 | 0.2 |
| $SiO_2$ | 44 | 59 | 38 | 46 | 56 | 47 | 54 | 23 | 54 | 43 | 17 | 47 | 54 | 48 | 44 | 40 | 43 | 52 |
| $PO_4$ | 2.6 | <1 | <1 | 1.7 | 2.0 | 2.3 | 2.0 | <1 | <1 | <1 | 1.2 | 1.2 | 2.6 | 1.5 | 2.0 | 2.3 | <1 | 2.0 |
| pH | 6.0 | 6.2 | 6.2 | 6.0 | 6.2 | 6.3 | 6.1 | 6.4 | 6.2 | 6.3 | 6.3 | 6.2 | 6.0 | 6.2 | 6.5 | 6.2 | 6.3 | 6.5 |
| $\frac{Na.100}{Na+Ca+Mg}$ | 54 | 64 | 62 | 48 | 46 | 52 | 41 | 65 | 31 | 43 | 63 | 49 | 32 | 37 | 52 | 52 | 51 | 48 |
| $\frac{Ca.100}{Na+Ca+Mg}$ | 24 | 19 | 21 | 17 | 21 | 24 | 32 | 18 | 37 | 31 | 18 | 27 | 32 | 32 | 25 | 22 | 19 | 13 |
| $\frac{Mg.100}{Na+Ca+Mg}$ | 22 | 17 | 17 | 35 | 33 | 24 | 27 | 17 | 32 | 26 | 19 | 24 | 36 | 31 | 23 | 26 | 30 | 39 |
| $Cl/SO_4$ | 3.2 | 8.3 | 2.9 | 1.2 | 12 | 1.8 | 1.2 | 7.6 | 3.3 | 2.9 | 7.0 | 5.3 | 2.1 | 25 | 4.5 | 2.1 | 2.7 | 11 |
| $Cl/Br$ | 71 | 340 | 78 | 308 | 380 | 160 | 158 | 190 | 50 | 50 | 58 | 105 | 50 | 438 | 232 | 255 | 342 | 180 |
| $Na/Cl$ | 3.5 | 6.5 | 19 | 1.2 | 2.7 | 6.5 | 3.1 | 9.5 | 7 | 14 | 8.4 | 6 | 2.9 | 1.3 | 2 | 1.4 | 1 | 1 |

TABLE 1—Analyses of Carbonated Spring Waters
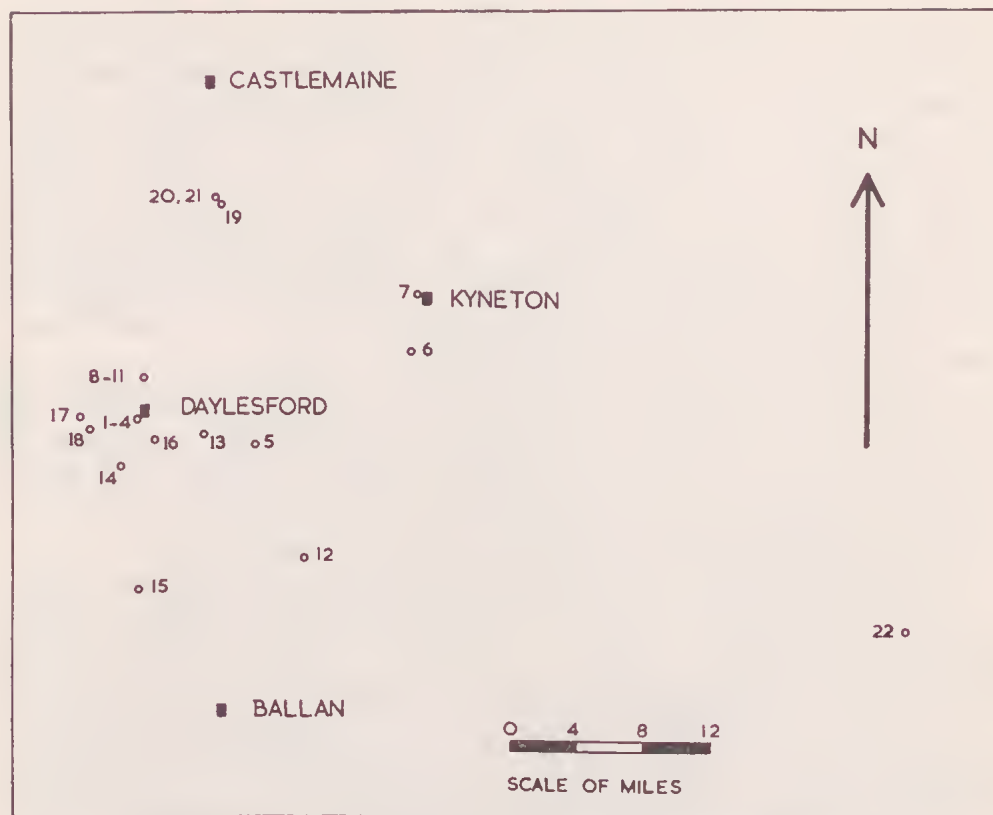
Fig. 1—Localities of carbonated spring waters with analyses Table 1.

sodium. These three, when recalculated to 100%, may be expressed on a ternary diagram, thus enabling various spring waters to be compared, for the other cations are quantitatively insignificant when compared with these three major components. A similar device is not possible for the anions because of the high carbonation.

## Discussion

There is no obvious relationship between carbonate content and either the major cations or anions. The inference is that the carbonation of these waters is a totally separate process from the addition of these other ions. Carbonate content affects the pH only slightly, but free evolution of carbon dioxide is sufficient to cause a rise of $0.2$-$0.3$ pH units in twelve hours. This increase is partially responsible for the deposition of hydrated iron oxides from the waters, on standing. The full mechanism of precipitation is not as obvious as it would seem, for it still occurs in sealed containers. The cause is not biological, for waters which have been treated with biological depressants still precipitate. It seems that a photochemical reaction is involved for deposition is more rapid in light.

The other major anions, chloride and sulphate, appear slightly inter-related with ratios $Cl/SO_4$ ranging generally from under 2 to over 4 and hence are similar to those in rain and river waters. Samples with very high ratios frequently have higher sodium content, and the Na/Cl ratio in these is considerably lower

than in most other samples. This would indicate that the take up of sodium chloride is separate, in at least some samples, from the supply of sulphate. This cannot imply addition of sodium chloride from evaporite minerals or connate water. The solution of halite or similar evaporite minerals gives very high chloride/bromide ratios, since bromide is excluded from the lattices during crystallization (Kuhn, 1955; Stewart, 1963). Bromide contents are very low in all the samples, and for reliable data only those where chloride is above about 60 p.p.m. should be considered. In waters where halides are above about 60 p.p.m. the ratio Cl/Br is similar to that for oceanic, river and rain waters. The conclusion must be reached that there is no contribution to these waters from leached salts. It is suggested that the cause of the high $Cl/SO_4$ ratio for some samples is not excess chloride but deficit of sulphate resulting from the microbiological activity of sulphate reducing bacteria—*desulphovibrio* sp. (Kuznetsov, et al. 1963).

Boron and phosphate contents are low; the values are normal for underground and river waters. Silica contents are higher than normal river waters, but when the higher total content of dissolved solid is considered, and the influence of chloride on silica solubility (Van Lier et al., 1960), the silica values agree with normal surface and underground waters (White et al. 1963; Livingstone, 1963). The occurrence of traces of zinc and copper in some of the waters is believed to be a result of contamination by material used in the taps or pumps.

The data assembled in Table 1 are strongly against any contribution to these waters from vulcanism, for waters associated with this have quite different chemical compositions. The chloride/bromide ratio is higher (White and Waring, 1963) as also is the boron content; sulphate is higher due to conversion from hydrogen sulphide; silica is higher due to the increased solubility of amorphous silica (Krauskopf, 1956; White et al., 1963). While it might be argued that precipitation en route to the surface might remove certain constituents, e.g. silica, such a precipitate should scavenge much of the iron and manganese from solution and this does not appear to have occurred, for both elements are moderately high and to some extent are interdependent.

The degree of scatter of the points on the ternary diagram in Fig. 2 is very small when it is considered that scatter in closely associated springs (Hepburn 8-11 and Daylesford 1-4) is almost as great. Data from various rivers and streams (Anderson, 1945; Livingstone, 1963) have been plotted on this ternary diagram and the overlap with the field covered by the spring water is quite marked. Perhaps more pertinent still is the data obtained from Wattle Gully Gold mine at Chewton. Water from a spring encountered in drilling at 1600 ft below the surface, when compared with seepage water from about 900 ft depth shows considerable advancement towards the Ca-Mg base in Fig. 2. It is not necessary to appeal to leaching of basalt to provide the additional calcium and magnesium in this case, for the rocks are sedimentary shales and sandstones of Ordovician age, apart from an occasional monchiquite dyke. By analogy, the contribution from leached basalt to the carbonated springs may also be quite small.

The origin of the considerable volume of carbon dioxide in these springs is not difficult to explain. The black Ordovician shales in these areas contain abundant organic material. Oxidation of this material by meteoric water containing oxygen would give carbon dioxide. Oxidation of pyrite would give hydrogen sulphide, which in turn would quite readily give sulphate by the action of thio bacteria. This is a process known to take place extensively (Kuznetsov et al., 1963). Under this hypothesis, carbonated waters should be much more common in the region if the process took place at shallow depths. Since this is not observed, the conclusion
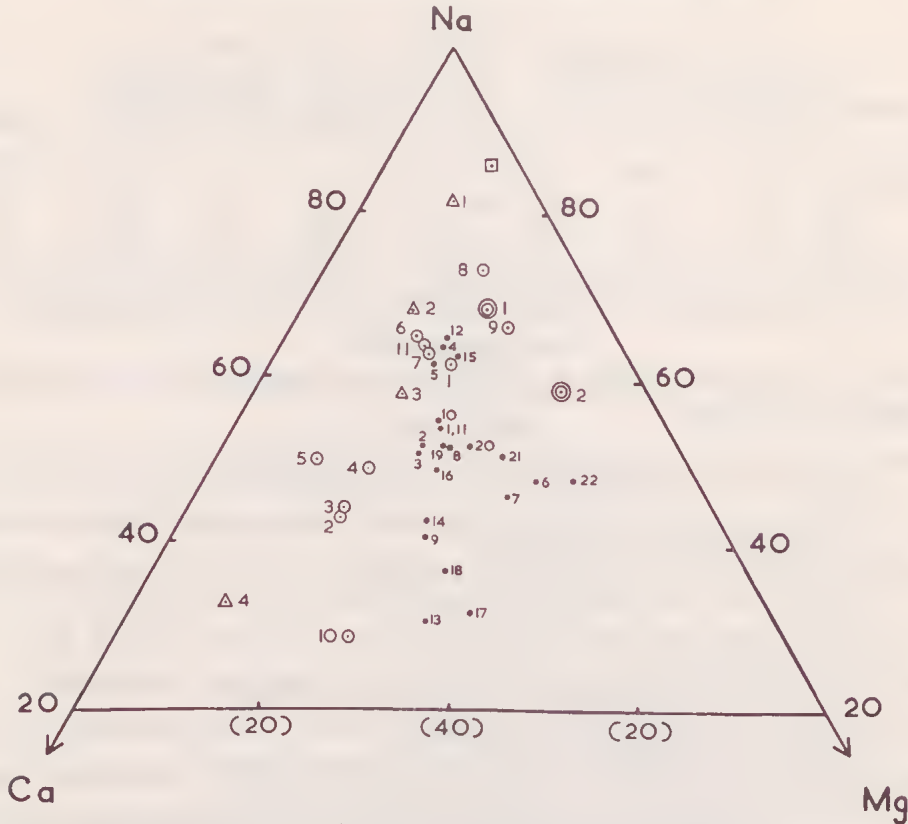
Fig. 2—Portion of the ternary diagram Na, Ca, Mg. Individual samples have been plotted as a percentage of the total Na + Ca + Mg for each analysis.

▣   average composition of sea water (Goldberg, 1963).
△   composition of rain waters: 1 = Bridgewater, 2 = Kyneton, 3 = Charlton, 4 = Merbein. (Values from Hutton & Leslie, 1958).
⊙   composition of various river and stream waters: 1 = O'Shannassy, 2 = Hotham, 3 = Kiewa, 4 = Delatite, 5 = Buffalo, 6, 7 = Yarra, 8 = Coleraine, 9 = Little River, 10 = Murray (Tocumwal), 11 = Murray (Murray Bridge) (Values from Anderson, 1941, 1945).
◎   Wattle Gully gold mine, Chewton: 1 = seepage at 900', 2 = spring at 1600'.
●   = carbonated springs with localities as in Fig. 1 and Table 1.

must be reached that the carbonated springs represent quite deep-seated sources of water which have come to the surface via faults or crush-zones. Their high carbon dioxide content would be enhanced because of higher solubility at high hydro-static pressure, and their escape to the surface would be via slow seepage rather than direct vents. The increasing salinity of the waters compared with rain water is explained by the theory of ion filtration via charged clay membranes whereby subterranean waters increase in salinity with depth (Bredehoeft et al., 1963). The movement towards the base of the diagram in Fig. 2 may be taken as a measure of the contribution from material dissolved from the rocks through which any individual spring flows.

F2

TABLE 2

*Comparison of carbonated spring waters sampled at intervals*

| Locality | Ca | | | | Mg | | | |
|---|---|---|---|---|---|---|---|---|
| | 1963 | 1964 | 1965 | 1966 | 1963 | 1964 | 1965 | 1966 |
| Kyneton (7) | 165 | 100 | 92 | 97 | — | 150 | 145 | 142 |
| Hepburn (8) | — | — | 141 | 155 | 131 | — | 144 | 133 |
| (9) | 175 | 195 | 154 | 171 | 128 | 106 | 126 | 116 |
| (10) | 141 | 144 | 141 | — | 114 | 107 | 127 | — |
| (11) | 127 | 136 | 124 | 120 | 91 | 128 | 116 | 99 |

\* The numbers in brackets are those used in Table 1. Values are given in parts per million.

## Acknowledgements

## References

ANDERSON, V. G., 1941. The origin of the dissolved inorganic solids in natural water with special reference to the O'Shannassy river catchment, Victoria. *J. Aust. Chem. Inst.* 8: 130-150.

————, 1945. Some effects of atmospheric evaporation and transpiration on the composition of natural waters. *Ibid.* 12: 41-68, 83-98.

BREDEHOEFT, J. D., BLYTH, C. R., WHITE, W. A., and MAXEY, G. B., 1963. Possible mechanism for concentration of brines in sub-surface formations. *Bull. Amer. Assn. Petrol. Geol.* 47: 257-269.

GOLDBERG, E. D., 1963. The Oceans as a Chemical System. In *"The Sea"*, Vol. 2, Ed. M. N. Hill, Interscience, 3-25.

HUTTON, J. T., and LESLIE, T. I., 1958. Accession of non-nitrogenous ions dissolved in rain water to soils in Victoria. *Aust. Jour. Agric. Res.* 9: 492-507.

KRAUSKOPF, K. B., 1956. Dissolution and precipitation of silica at low temperatures. *Geochim. et Cosmochim. Acta.* 10: 1-26.

KUHN, R., 1955. Mineralogische fragen der in den kalisalzlagerstätten vorkommenden salze. Internat. Kali-Institut. Bern, Switzerland. *Kalium Symposium.*

KUZNETSOV, S. I., IVANOV, M. V., and LYALIKOVA, N. N., 1963. *Introduction to geological microbiology.* (English translation) McGraw-Hill, New York. 252 pp.

LIVINGSTONE, D. A., 1963. Data of Geochemistry. G. Chemical composition of rivers and lakes. *U.S. Geol. Surv. Prof. Paper* 440G: 1-64.

MULLIN, J. B., and RILEY, J. P., 1955. The colorimetric determination of silicate with special reference to sea and natural waters. *Analyt. Chim. Acta.* 12: 162-176.

NEWBERY, J. C., 1867. Mineral waters of Victoria. *Trans. Roy. Soc. Vict.* 8: 278-283.

SHAPIRO, L., and BRANNOCK, W. W. Rapid analysis of silicate, carbonate and phosphate rocks. *U.S. Geol. Surv. Bull.* 1144 A: 1-56.

SKEATS, E. W., 1914. Mineral springs at or near Hepburn. *Bull. Geol. Surv. Vict.* No. 36: 1-20.

STEWART, F. H., 1963. Data of Geochemistry. Marine evaporites. *U.S. Geol. Surv. Prof. Paper* 440-Y: 1-52.

VAN LIER, J. A., DE BRUYN, P. L., and OVERBEEK, J. Th. G., 1960. The solubility of quartz. *J. Phys. Chem.* 64: 1675-1682.

VOGEL, A. I., 1961. *A textbook of quantitative inorganic analysis.* Longmans Green & Co., London. 1216 pp.

WELCHER, F. J., 1958. *The analytical uses of ethylenediamine-tetraacetic acid.* Van Nostrand, Princeton. U.S.A., 366 pp.

WHITE, D. E., HEM, J. D., and WARING, G. A., 1963. Data of Geochemistry. F. Chemical composition of sub surface waters. *U.S. Geol. Surv. Prof. Paper* 440F: 1-67.

WHITE, D. E., and WARING, G. A., 1963. Data of Geochemistry. K. Volcanic emanations. *U.S. Geol. Surv. Prof. Paper* 440K: 1-29.

WHITELAW, H. S., and BARAGWANATH, W., 1923. The Daylesford gold field. IV Mineral Springs. *Bull. Geol. Surv. Vict.* No. 42: 93-94.

WILLIS, J. B., 1963. Atomic absorption spectroscopy. In *Methods of Biochemical Analysis* (Glick, D., Ed.) Interscience, New York. Vol. 11: 1-67.

WILSON, C. L., and WILSON, D. W., 1962. *Comprehensive analytical chemistry.* Elsevier, Amsterdam. Vol. 1C. 728 pp.